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GAS–LIQUID CHROMATOGRAPHIC ANALYSES

VII. GAS CHROMATOGRAPHY OF C_1–C_8 n-ALKYL ACETATES AND METHYL ESTERS OF ALIPHATIC C_2–C_9 n-CARBOXYLIC ACIDS AND CERTAIN OF THEIR MONOCHLORINATED DERIVATIVES ON CARBOWAX 20M AND SE-30 GLASS CAPILLARY COLUMNS

ILPO O. O. KORHONEN

Department of Chemistry, University of Jyväskylä, Kyllikinkatu 1–3, SF-40100 Jyväskylä 10 (Finland)

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SUMMARY

The gas chromatography of mixtures of n-alkyl acetates (CH_3COOR, $R = C_1$–C_8) and methyl esters of aliphatic n-carboxylic acids ($R'COOCH_3$, $R' = C_1$–C_8) and certain of their monochlorinated derivatives has been studied on Carbowax 20M and SE-30 glass capillary columns under the same operating conditions. The separation of the isomeric monochlorinated esters was complete on Carbowax 20M, whereas on SE-30 the peaks of 6- and 7-chlorooctyl acetates and methyl ($\omega - 1$)- and ($\omega - 2$)-chlorooctanoates and -nonanoates partly overlapped. The complete separation of the mixtures could not be achieved, however, on Carbowax 20M, in spite of the use of various operating conditions. The results show that all 44 individual components can be separated using columns with polar and non-polar stationary phases. The relative retention times for the compounds are given and the elution order is discussed. The retention times of alkyl acetates are always shorter than those of methyl esters with the same chain lengths ($R = R'$). The greatest disparities are observed between the retention behaviours of 1-chloroalkyl acetates and methyl 2-chloro esters, whereas the effect of a chlorine substituent further away seems to be negligible.

INTRODUCTION

The gas chromatographic (GC) retention behaviour of homologous saturated esters ($R'COOR$) on polar and non-polar stationary phases has been extensively studied by Haken and co-workers[1-6]. The number of carbon atoms of the acid (R') and alcohol chains (R) varied between 0 and 6 and between 1 and 8, respectively. Schomburg[7] determined retention indices for a large number of aliphatic methyl esters using a capillary column with a non-polar stationary phase.

There have been few studies on the GC of halogenated esters, however. Recently, we have reported GC separations of the mixtures with a wide range of chain lengths of methyl and chloromethyl monochloro esters of aliphatic carboxylic

acids[8-13]. In addition, the GC of some di- and polyhalogenated methyl esters of aliphatic short-chain carboxylic acids has been studied[14-18].

In this paper the GC of a number of homologous series of aliphatic n-esters and their monochlorinated derivatives is reported. The parent esters were CH_3COOR and $R'COOCH_3$, where the carbon number of the alcohol (R) and acid (R') chains varied between 1 and 8. The separations of the mixtures of parent esters and their isomeric monochlorinated derivatives (the chlorine substituent at R and R'), 44 compounds altogether, were carried out on polar Carbowax 20M and non-polar SE-30 glass capillary columns under the same operating conditions. The relative retention times for the compounds are given and the retention behaviour of alkyl acetates and methyl esters with the same chain lengths (R = R') is compared.

EXPERIMENTAL

Preparation of esters

Methyl, ethyl, n-propyl, n-butyl and n-pentyl acetates were commercial products (Fluka, Buchs, Switzerland). n-Hexyl, n-heptyl and n-octyl acetates were prepared[19] from the corresponding commercial alcohols (Fluka) and acetyl chloride (Fluka). Chloromethyl acetate was synthesized from acetyl chloride and paraformaldehyde in the presence of a trace amount of zinc chloride[20]. The other monochlorinated alkyl acetates were prepared by chlorination of the corresponding parent esters as described earlier[21].

Methyl esters of aliphatic C_3–C_9 n-carboxylic acids were prepared by the usual sulphuric acid-catalysed esterification of commercial acids (Fluka). Methyl chloroacetate was obtained from the commercial chloroacetic acid (Fluka) by esterification and the other methyl monochloro esters were prepared as described earlier[11].

The crude chlorination mixtures of isomeric monochloro esters were used for GC analyses. The additional peaks illustrated in the figures are unidentified polychloro esters.

Gas chromatography

GC analyses were carried out with a Varian Model 2400 gas chromatograph, adapted for glass capillary work, and with a Perkin-Elmer Sigma 3 instrument under the following operating conditions: injector temperature, 220°C; flame-ionization detector, 240°C (hydrogen and air flow-rates 40 and 300 ml/min, respectively); nitrogen carrier gas flow-rate, 1 ml/min; splitting ratio, 1:25; and chart speed, 10 mm/min. The following columns were used: a 5% Carbowax 20M glass capillary column (22 m × 0.30 mm I.D.), prepared in our laboratory[18], and a vitreous-silica SE-30 wall-coated open-tubular (WCOT) column (25 m × 0.22 mm I.D.), supplied by Scientific Glass (North Melbourne, Australia). The column temperature was programmed from 50°C at 6°C/min until elution of peaks ceased.

RESULTS AND DISCUSSION

It is necessary to use temperature programming for the analysis of a mixture with a wide range of chain lengths so that the short-chain compounds can be separated from the solvent peak and the long-chain isomers will be eluted sharply[10-12].
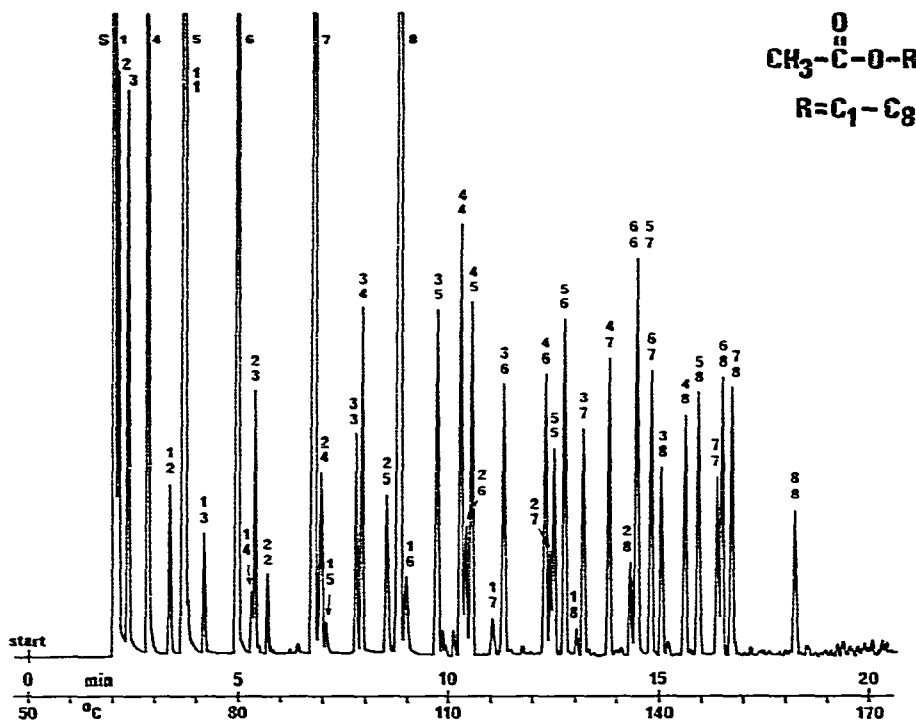
$$CH_3-\overset{\overset{\textstyle O}{\|}}{C}-O-R$$

$$R=C_1-C_8$$

Fig. 1. Chromatogram of the mixture of C_1–C_8 n-alkyl acetates and their monochlorinated derivatives on a Carbowax 20M glass capillary column. S = solvent. Compounds: 1–8 = parent esters from methyl acetate (1) to n-octyl acetate (8); the upper numbers = position of the chlorine substituent, the lower numbers = alcohol chain length (e.g., $\frac{3}{6}$ = 3-chlorohexyl acetate). Additional peaks are unidentified polychloro isomers, formed in the chlorinations.

The gas chromatograms of the mixture of C_1–C_8 n-alkyl acetates and their monochlorinated derivatives obtained on Carbowax 20M and SE-30 are illustrated in Figs. 1 and 2, respectively. The isomeric monochlorinated n-alkyl acetates are eluted in direct order from the 1-chloro to the ω-chloro compound, as are the corresponding methyl[11] and chloromethyl derivatives[12], the retention times increasing continuously as the chlorine substituent becomes further removed from the ether oxygen atom. Table I gives the relative retention times for the compounds, which are tabulated relative to the unchlorinated alkyl acetates (parent esters) = 1.00 and relative to 2-chlorobutyl acetate = 1.00. The retention is also expressed as the ratios of the retention times of the compounds on SE-30 to those on Carbowax 20M. Although the GC analyses of the chlorination products of some alkyl acetates have been reported earlier[22–24], the present results appear to be the first detailed GC data for these compounds.

Figs. 1 and 2 show that the separation of the isomeric monochlorinated alkyl acetates is complete on Carbowax 20M, whereas on SE-30 the isomers are eluted close to each other, leading to poor separation of the 6-chloro- and 7-chlorooctyl acetates. The polarity of the isomeric monochlorinated alkyl acetates increases with increase in the distance between the ether oxygen atom and the chlorine substituent,
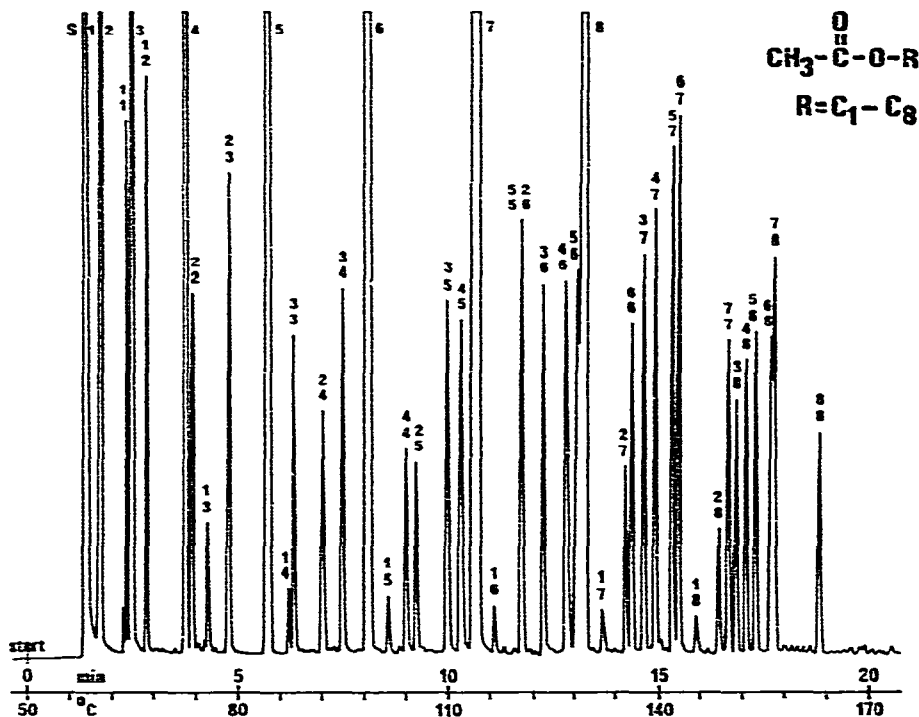
Fig. 2. Chromatogram of the mixture of C_1–C_8 n-alkyl acetates and their monochlorinated derivatives on an SE-30 quartz capillary column. S = Solvent. Compounds as in Fig. 1.

which leads to better separation of the isomers on a polar than on a non-polar column.

Complete separation of the mixture of all 44 alkyl acetates could not be achieved, however. On Carbowax 20M the peak of methyl acetate was overlapped by that of the solvent, pentyl and chloromethyl esters were coincident, 1-chlorobutyl and 2-chloropropyl isomers were poorly separated and 6-chlorohexyl and 5-chloroheptyl acetates were completely overlapped. On the other hand, the following compounds were overlapped on SE-30: methyl acetate and solvent, 5-chloropentyl and 2-chlorohexyl esters, 5-chlorohexyl and octyl isomers and 6-chloro- and 7-chlorooctyl acetates. Hence, methyl acetate was the only compound that overlapped the solvent on both columns, so that all 44 individual components of the mixture can be separated using both polar and non-polar stationary phases and methyl acetate as solvent.

Different elution orders of alkyl acetates are observed on the polar and the non-polar column. Fig. 3 illustrates the retention times for the esters relative to 2-chlorobutyl acetate, which appeared nearly at the same time on both columns (Table I). As can be seen, the greatest disparities are observed between the relative retention times of the parent esters and the ω-chloro isomers. The ω-chloro esters have relatively long elution times on Carbowax 20M, 1-chloroethyl and 2-chloropropyl acetates being eluted before the short-chain chloromethyl and 2-chloroethyl isomers, respectively. On SE-30, however, the esters are eluted in the reverse order. The same effect
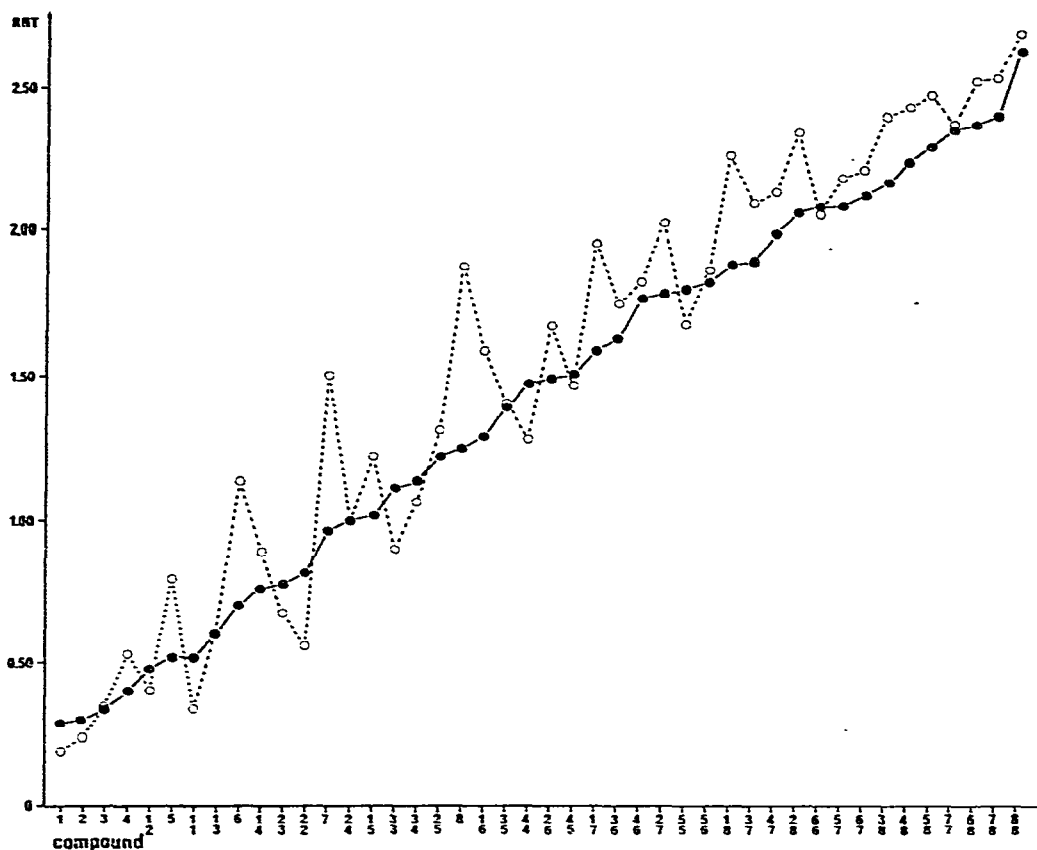
Fig. 3. Relative retention times (RRT) for C_1–C_8 n-alkyl acetates and their monochlorinated derivatives on Carbowax 20M (●—●) and SE-30 (O ——— O) columns. Relative retention time for 2-chlorobutyl acetate ($\frac{1}{2}$) taken as 1.00 (see Table I, columns 3 and 7).

has been reported earlier with methyl mono- and dichloro esters of acetic, propanoic and butanoic acids[18]. The short-chain (ω − 1)-chloro isomers also have higher retention times on the polar column up to and including a chain length of C_5. In general, the retention times of the compounds increase with increasing polarity of the stationary phase[4]. However, for long chain lengths (C_6–C_8) and for other isomers higher relative retention times are observed on SE-30, as silica WCOT columns have higher efficiency than glass capillary columns[13]. This can be seen from the higher relative retention times of ω-chloroheptyl and ω-chlorooctyl acetates on SE-30 (Table I, Fig. 3).

The GC of methyl esters of aliphatic C_2–C_{18} n-carboxylic acids and their monochlorinated derivatives has been reported earlier on a long (90-m) glass capillary column coated with Carbowax 20M stationary phase[11]. To compare the GC behaviour of both series of esters, the separations of methyl esters of aliphatic C_2–C_9 n-carboxylic acids and their monochlorinated derivatives were carried out under the same operating conditions as for the n-alkyl acetates, the mixture being analysed on

TABLE I

RELATIVE RETENTION TIMES (RRT) FOR ALIPHATIC C_1, C_8 n-ALKYL ACETATES AND THEIR MONOCHLORINATED DERIVATIVES ON CARBOWAX 20M AND SE-30 GLASS CAPILLARY COLUMNS

CH_3COOR acetates	Column Carbowax 20M				SE-30				
	Retention time*	RRT**	RRT***	RRT''	Retention time*	RRT**	RRT***	RRT'	RRT''
Methyl	2.00	1.00	0.29	1.00	1.31	1.00	0.19	0.66	1.00
Chloromethyl	3.60	1.80	0.52	0.75	2.34	1.79	0.34	0.65	0.83
Ethyl	2.10	1.00	0.30	0.97	1.69	1.00	0.24	0.80	0.88
1-Chloroethyl	3.31	1.58	0.48	0.84	2.80	1.66	0.40	0.85	0.85
2-Chloroethyl	5.65	2.69	0.82	0.95	3.89	2.30	0.56	0.69	0.93
Propyl	2.34	1.00	0.34	0.98	2.46	1.00	0.35	1.05	0.96
1-Chloropropyl	4.15	1.77	0.60	0.85	4.25	1.73	0.61	1.02	0.88
2-Chloropropyl	5.35	2.29	0.78	0.96	4.72	1.92	0.68	0.88	0.96
3-Chloropropyl	7.74	3.31	1.12	1.00	6.29	2.56	0.90	0.81	0.98
Butyl	2.79	1.00	0.40	0.97	3.71	1.00	0.53	1.33	0.95
1-Chlorobutyl	5.29	1.90	0.77	0.85	6.20	1.67	0.89	1.17	0.90
2-Chlorobutyl	6.90	2.47	1.00	0.95	6.97	1.88	1.00	1.01	0.96
3-Chlorobutyl	7.87	2.82	1.14	0.99	7.43	2.00	1.07	0.94	0.97
4-Chlorobutyl	10.24	3.67	1.48	0.98	8.97	2.42	1.29	0.88	0.97
Pentyl	3.60	1.00	0.52	0.96	5.61	1.00	0.80	1.56	0.96
1-Chloropentyl	7.06	1.96	1.02	0.87	8.56	1.53	1.23	1.21	0.92
2-Chloropentyl	8.47	2.35	1.23	0.95	9.20	1.64	1.32	1.09	0.97
3-Chloropentyl	9.65	2.68	1.40	0.99	9.92	1.77	1.42	1.03	0.97
4-Chloropentyl	10.45	2.90	1.51	0.97	10.23	1.82	1.47	0.98	0.97
5-Chloropentyl	12.44	3.46	1.80	0.98	11.70	2.09	1.68	0.94	0.97

Hexyl	4.90	1.00	0.71	0.96	7.98	1.00	1.14	0.96
1-Chlorohexyl	8.96	1.83	1.30	0.89	11.08	1.39	1.59	0.94
2-Chlorohexyl	10.35	2.11	1.50	0.95	11.70	1.47	1.68	0.98
3-Chlorohexyl	11.23	2.29	1.63	0.98	12.21	1.53	1.75	0.97
4-Chlorohexyl	12.20	2.49	1.77	0.97	12.76	1.60	1.83	0.97
5-Chlorohexyl	12.65	2.58	1.83	0.98	13.00	1.63	1.87	0.98
6-Chlorohexyl	14.39	2.94	2.09	0.97	14.33	1.80	2.06	0.98
Heptyl	6.69	1.00	0.97	0.97	10.52	1.00	1.51	0.97
1-Chloroheptyl	11.00	1.64	1.59	0.90	13.63	1.30	1.96	0.95
2-Chloroheptyl	12.34	1.84	1.79	0.96	14.20	1.35	2.04	0.98
3-Chloroheptyl	13.13	1.96	1.90	0.98	14.61	1.39	2.10	0.98
4-Chloroheptyl	13.73	2.05	1.99	0.97	14.89	1.42	2.14	0.98
5-Chloroheptyl	14.39	2.15	2.09	0.97	15.29	1.45	2.19	0.98
6-Chloroheptyl	14.73	2.20	2.13	0.98	15.44	1.47	2.22	0.98
7-Chloroheptyl	16.30	2.44	2.36	0.98	16.61	1.58	2.38	0.99
Octyl	8.70	1.00	1.26	0.97	13.10	1.00	1.88	0.98
1-Chlorooctyl	13.01	1.50	1.89	0.92	15.82	1.21	2.27	0.96
2-Chlorooctyl	14.25	1.64	2.07	0.97	16.40	1.25	2.35	0.98
3-Chlorooctyl	14.97	1.72	2.17	0.98	16.81	1.28	2.41	0.98
4-Chlorooctyl	15.55	1.79	2.25	0.98	17.04	1.30	2.44	0.98
5-Chlorooctyl	15.85	1.82	2.30	0.97	17.28	1.32	2.48	0.98
6-Chlorooctyl	16.42	1.89	2.38	0.98	17.62	1.34	2.53	0.98
7-Chlorooctyl	16.65	1.91	2.41	0.98	17.69	1.35	2.54	0.99
8-Chlorooctyl	18.15	2.09	2.63	0.99	18.76	1.43	2.69	0.99

* Absolute retention times (min) were measured from sample injection (Figs. 1 and 2).

** Relative retention times for unchlorinated alkyl acetates (parent esters) taken as 1.00.

*** Relative retention time for 2-chlorobutyl acetate taken as 1.00.

§ Relative retention times for compounds on Carbowax 20M taken as 1.00.

§§ Relative retention times for the corresponding methyl esters taken as 1.00; absolute retention times for methyl esters are given in Table II (e.g., the value 0.97 for 4-chlorohexyl acetate is relative to methyl 5-chloroheptanoate).
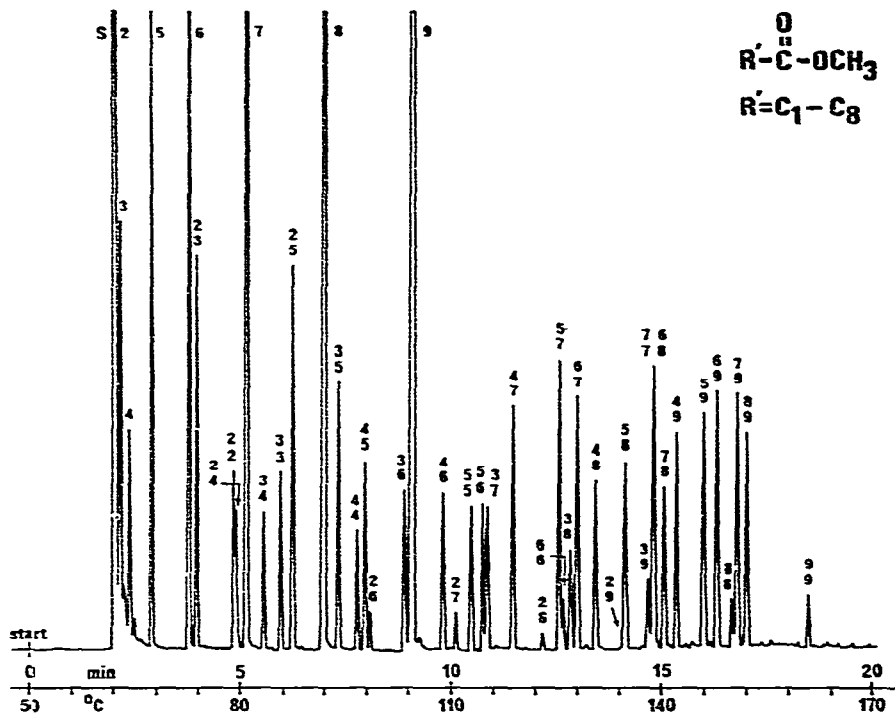
Fig. 4. Chromatogram of the mixture of methyl esters of aliphatic C_2–C_9 n-carboxylic acids and their monochlorinated derivatives on a Carbowax 20M glass capillary column. S = Solvent. Compounds: 2–9 = parent methyl esters from methyl acetate (2) to methyl nonanoate (9): the upper numbers = position of the chlorine substituent, the lower numbers = acid chain length (e.g., $\frac{2}{6}$ = methyl 3-chlorohexanoate). Additional peaks are unidentified polychloro isomers, formed in the chlorinations.

Carbowax 20M (Fig. 4) and on SE-30 (Fig. 5). The retention data for these esters are shown in Table II relative to the parent esters = 1.00, to methyl 3-chloropentanoate (Fig. 6) and to the corresponding compounds analysed on Carbowax 20M.

Earlier GC studies showed that mixtures of even- and odd-carbon-number esters can be separated[11]. GC of the mixture of all 44 esters (Figs. 4 and 5) resulted in some overlapping peaks. The polar column provided a more efficient separation of isomeric monochloro esters, but the following components of the mixture overlapped: methyl acetate and solvent, methyl chloroacetate and 2-chlorobutanoate, methyl 2-chlorononanoate and 5-chlorooctanoate and methyl 7-chloroheptanoate and 6-chlorooctanoate. Fig. 5 shows that SE-30 separated only partly the isomeric ($\omega - 1$)-chloro and ($\omega - 2$)-chloro esters of octanoic and nonanoic acids. Poor separations of methyl 6-chloroheptanoate and methyl nonanoate and of methyl 3-chlorooctanoate and 7-chloroheptanoate are observed. Methyl 5-chloropentanoate and 2-chlorohexanoate, on the other hand, are nearly completely overlapped.

As with chlorinated n-alkyl acetates, the individual components of the mixture of methyl esters can be separated using both polar and non-polar columns. In addition, Table II and Fig. 6 show the same GC behaviour of the compounds as mentioned above for the corresponding alkyl acetates.
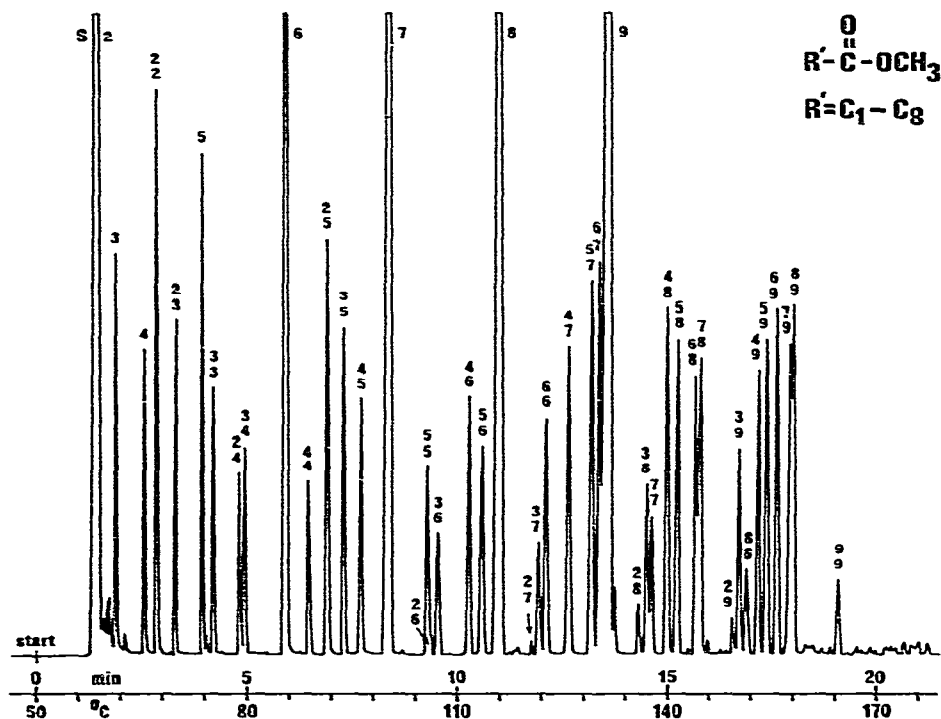
Fig. 5. Chromatogram of the mixture of methyl esters of aliphatic C_2–C_9 n-carboxylic acids and their monochlorinated derivatives on an SE-30 quartz capillary column. S = Solvent. Compounds as in Fig. 4.

Fig. 7 illustrates the separation of the combined mixture of the parent C_1–C_8 n-alkyl acetates and methyl esters of aliphatic C_2–C_9 n-carboxylic acids on SE-30. The compounds are eluted in the same order as on the polar column. It was previously observed that an increase in the alcohol carbon chain length (R) had a greater effect on the retention than a corresponding increase in the acid carbon chain length (R′)[1,3,4]. Fig. 7 shows that the retention times of the parent methyl esters (R′COOCH₃) are always longer than those of the corresponding alkyl acetates (CH₃COOR) with the same chain length (R = R′). The results are in general agreement with those of Haken and co-workers, who analysed the esters on the packed columns with several stationary phases[1–4]. According to their results, however, reversed elution orders of some esters on OV-210[3] (R = R′ = 2, 3, 4, 5) and QF-1[4] (R = R′ = 2, 3, 5) are observed, the methyl ester being eluted before the acetate ester.

The GC analysis of combined mixtures of the corresponding chlorinated isomeric esters resulted in overlapping peaks, however, particularly with long-chain esters. As can be seen from Table I (columns 4 and 9), greater relative retention times are also observed for chlorinated methyl esters. Chlorine substituents in the α-positions give rise to the greatest disparities between the retention behaviours of the esters, having a greater effect on the retention in the alcohol chain than in the acid chain. This can be seen from the relatively short retention times of 1-chloroalkyl acetates compared with those of methyl 2-chloro esters. The short retention times of

TABLE II

RELATIVE RETENTION TIMES (RRT) FOR METHYL ESTERS OF ALIPHATIC C_2–C_9 n-CARBOXYLIC ACIDS AND THEIR MONOCHLORINATED DERIVATIVES ON CARBOWAX 20M AND SE-30 GLASS CAPILLARY COLUMNS

$R'COOCH_3$ methyl esters	Column						
	Carbowax 20M			SE-30			
	Retention time*	RRT**	RRT***	Retention time*	RRT**	RRT***	RRT[§]
Acetate	2.00	1.00	0.27	1.31	1.00	0.18	0.66
Chloroacetate	4.83	2.42	0.66	2.82	2.15	0.39	0.58
Propanoate	2.16	1.00	0.30	1.91	1.00	0.26	0.88
2-Chloropropanoate	3.94	1.82	0.54	3.28	1.72	0.45	0.83
3-Chloropropanoate	5.93	2.75	0.81	4.19	2.19	0.58	0.71
Butanoate	2.39	1.00	0.33	2.57	1.00	0.35	1.08
2-Chlorobutanoate	4.87	2.04	0.67	4.81	1.87	0.66	0.99
3-Chlorobutanoate	5.55	2.32	0.76	4.91	1.91	0.68	0.88
4-Chlorobutanoate	7.76	3.25	1.06	6.44	2.51	0.89	0.83
Pentanoate	2.88	1.00	0.40	3.92	1.00	0.54	1.36
2-Chloropentanoate	6.21	2.16	0.85	6.87	1.75	0.95	1.11
3-Chloropentanoate	7.29	2.53	1.00	7.25	1.85	1.00	0.99
4-Chloropentanoate	7.93	2.75	1.09	7.65	1.95	1.06	0.96
5-Chloropentanoate	10.45	3.63	1.43	9.25	2.36	1.28	0.89
Hexanoate	3.75	1.00	0.51	5.85	1.00	0.81	1.56
2-Chlorohexanoate	8.07	2.15	1.11	9.35	1.60	1.29	1.16
3-Chlorohexanoate	8.87	2.37	1.22	9.52	1.63	1.31	1.07
4-Chlorohexanoate	9.79	2.61	1.34	10.25	1.75	1.41	1.05
5-Chlorohexanoate	10.75	2.87	1.47	10.55	1.80	1.46	0.98
6-Chlorohexanoate	12.65	3.37	1.74	12.08	2.06	1.67	0.95
Heptanoate	5.10	1.00	0.70	8.28	1.00	1.14	1.62
2-Chloroheptanoate	10.11	1.98	1.39	11.78	1.42	1.62	1.17
3-Chloroheptanoate	10.85	2.13	1.49	11.91	1.44	1.64	1.10
4-Chloroheptanoate	11.45	2.25	1.57	12.59	1.52	1.74	1.10
5-Chloroheptanoate	12.52	2.45	1.72	13.11	1.58	1.81	1.05
6-Chloroheptanoate	12.95	2.54	1.78	13.30	1.61	1.83	1.03
7-Chloroheptanoate	14.76	2.89	2.02	14.60	1.76	2.01	0.99
Octanoate	6.90	1.00	0.95	10.84	1.00	1.50	1.57
2-Chlorooctanoate	12.17	1.76	1.67	14.29	1.32	1.97	1.17
3-Chlorooctanoate	12.80	1.86	1.76	14.44	1.33	1.99	1.13
4-Chlorooctanoate	13.38	1.94	1.84	14.91	1.38	2.06	1.11
5-Chlorooctanoate	14.12	2.05	1.94	15.15	1.40	2.09	1.07
6-Chlorooctanoate	14.76	2.14	2.02	15.60	1.44	2.15	1.06
7-Chlorooctanoate	15.02	2.18	2.06	15.71	1.45	2.17	1.05
8-Chlorooctanoate	16.62	2.41	2.28	16.81	1.55	2.32	1.01

TABLE II *(continued)*

$R'COOCH_3$ methyl esters	Column						
	Carbowax 20M			SE-30			
	Retention time*	RRT**	RRT***	Retention time*	RRT**	RRT***	RRT$
Nonanoate	9.00	1.00	1.23	13.40	1.00	1.85	1.49
2-Chlorononanoate	14.09	1.57	1.93	16.52	1.23	2.28	1.17
3-Chlorononanoate	14.66	1.63	2.01	16.69	1.25	2.30	1.14
4-Chlorononanoate	15.30	1.70	2.10	17.10	1.28	2.36	1.12
5-Chlorononanoate	15.94	1.77	2.19	17.30	1.29	2.39	1.09
6-Chlorononanoate	16.26	1.81	2.23	17.55	1.31	2.42	1.08
7-Chlorononanoate	16.72	1.86	2.29	17.82	1.33	2.46	1.07
8-Chlorononanoate	16.96	1.88	2.33	17.90	1.34	2.47	1.06
9-Chlorononanoate	18.42	2.05	2.53	19.00	1.42	2.62	1.03

 * Absolute retention times (min) were measured from sample injection (Figs. 4 and 5).
 ** Relative retention times for unchlorinated methyl esters (parent esters) taken as 1.00.
 *** Relative retention times for methyl 3-chloropentanoate taken as 1.00.
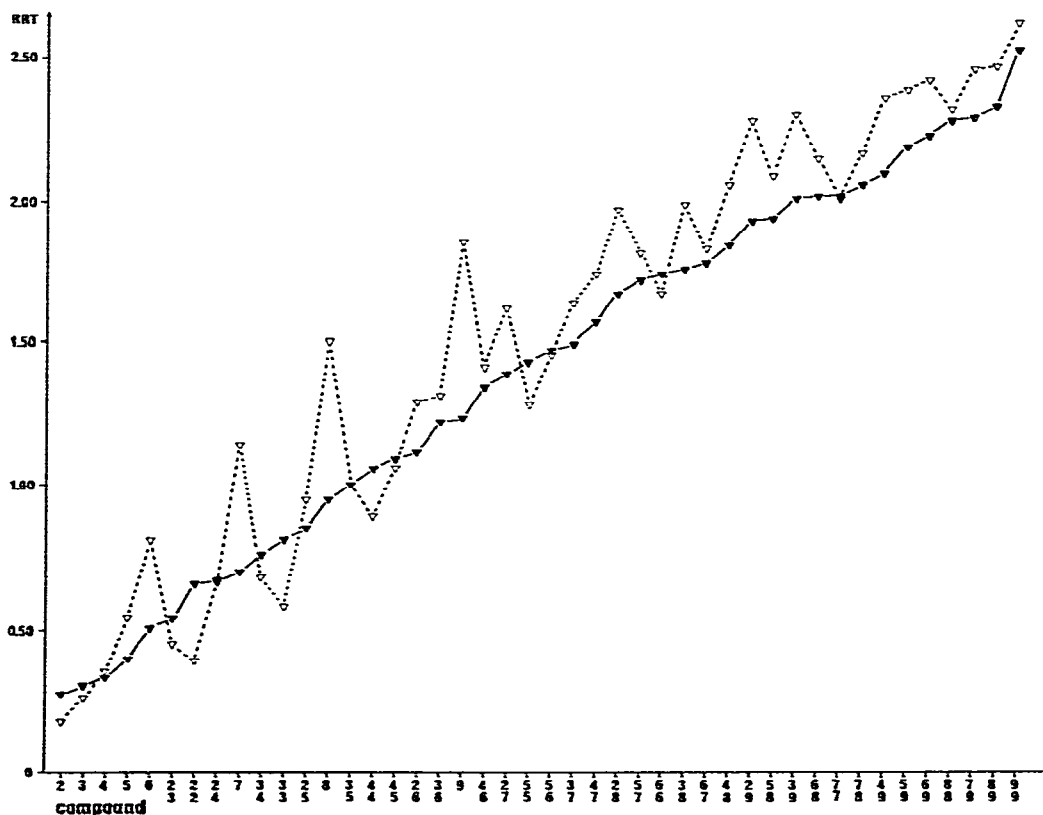 $ Relative retention times for compounds on Carbowax 20M taken as 1.00.

Fig. 6. Relative retention times (RRT) for methyl esters of aliphatic C_2–C_9 *n*-carboxylic acids and their monochlorinated derivatives on Carbowax 20M (▼—▼) and SE-30 (▽ – – – ▽) columns. Relative retention times for methyl 3-chloropentanoate ($\frac{3}{5}$) taken as 1.00 (see Table II, columns 3 and 6).
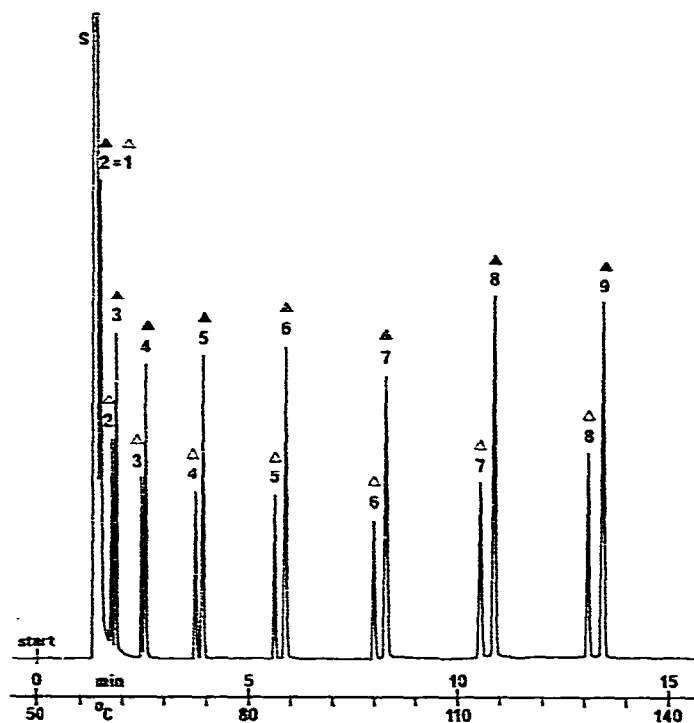
Fig. 7. Chromatogram of the mixture of C_1–C_8 n-alkyl acetates ($\triangle$) and methyl esters of C_2–C_9 n-carboxylic acids ($\blacktriangle$) on an SE-30 quartz capillary column. S = Solvent. Numbers on peaks = chain length.

chloromethyl 2-chloro esters, relative to the corresponding methyl esters, on a polar column has been reported previously[12]. The effect of chlorine substituents further away, in contrast, seems to be negligible. As expected, smaller disparities between the retention behaviours of the esters on SE-30 are observed.

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